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*Published in:*  
Journal of Petroleum Science and Engineering

*DOI:*  
[10.1016/j.petrol.2006.04.017](https://doi.org/10.1016/j.petrol.2006.04.017)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2007

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*  
van Elk, E. P., Versteeg, G. F., & van Loo, S. (2007). The removal of carbon dioxide with activated solutions of methyl-diethanol-amine. *Journal of Petroleum Science and Engineering*, 55(1), 135-145.  
<https://doi.org/10.1016/j.petrol.2006.04.017>

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# The removal of carbon dioxide with activated solutions of methyl-diethanol-amine

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Received 19 April 2005; accepted 26 April 2006

## Abstract

The (bulk) removal of carbon-dioxide (CO<sub>2</sub>) from industrial gases, e.g. natural gas, is usually realized with a reactive absorption technique in which (non-)aqueous solutions of alkanolamines are used.

From the absorption rate point of view, primary or secondary amines are preferred. However, in case the costs of regeneration are also taken into account, tertiary amines are much more attractive. In order to combine the specific properties of tertiary and primary/secondary alkanolamines respectively, mixtures of both types of compounds are used. A well known example is the activated methyl-di-ethanol-amine (MDEA)-process in which MDEA is mixed with (small amounts) of piperazine.

In this paper mixtures of MDEA with several activators, being primary and secondary amines, are studied with respect to the performance of CO<sub>2</sub> removal from natural gas. The absorption process in a tray column has been simulated. For a number of default cases the impact of the activator on the total number of trays has been calculated. From these simulations the optimal number of trays in combination with the amount of activator-addition can be established. Furthermore, insight is obtained on the mechanism of the absorption steps in mixed amine solutions. It is demonstrated that the working action of the accelerator, the fast reacting amine, is substantially influenced by the partial pressures of carbon dioxide in the gas mixture. Moreover, this effect is strongly depending on the molar fraction of the accelerator.

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**Keywords:** Carbon dioxide; Chemical absorption; Alkanolamines; Accelerators; Modelling

## 1. Introduction

The separation of gas impurities such as carbon-dioxide (CO<sub>2</sub>) and hydrogen-sulphide (H<sub>2</sub>S) from gas mixtures is an important operation in natural gas treating, petroleum refining, coal gasification and ammonia manufacturing industries. Since CO<sub>2</sub> is

regarded as a major greenhouse gas, contributing to global warming, there is a growing interest in developing technologies for capturing and sequestering large quantities of CO<sub>2</sub> produced from industrial sources such as fossil-fuel electric power generation facilities.

Gas absorption by chemical solvents such as aqueous solutions of alkanolamines is one of the most effective methods for CO<sub>2</sub> removal. This technology has been used in industry for over half a century. In modern gas treating industries mono-ethanol-amine (MEA), di-ethanol-amine (DEA) and methyl-di-ethanol-amine (MDEA) are the most commonly used alkanolamines.

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From the absorption rate point of view, primary (i.e. MEA) or secondary amines (i.e. DEA) are preferred. However, in case the costs of regeneration are taken into account, tertiary amines (i.e. MDEA) are much more attractive. In order to combine the specific properties of tertiary and primary/secondary alkanolamines respectively, mixtures of both types of compounds are used. A well known example is the activated MDEA-process in which MDEA is mixed with (small amounts) of piperazine.

In this paper combinations of an aqueous MDEA solution with several primary and secondary alkanolamines as accelerator are evaluated based on simulation of the performance in the absorption section of a gas treating plant. In contrary to piperazine, reaction kinetics, physical- and chemical properties of the evaluated accelerators are well established in open literature.

An absorption micro model has been developed describing the fluxes at the gas/liquid interface. This model has been integrated with an absorption macro model which describes overall gas absorption performance.

## 2. Model description

### 2.1. The macro/absorber model

The absorbers are calculated by a tray-to-tray procedure (Blauwhoff et al., 1985). The absorption column is considered as a series of ideally mixed (with respect to both gas and liquid phases) reactors, each corresponding to an actual tray (Fig. 1).

Process conditions and gas and liquid compositions are assumed to be uniform in each reactor. More sophisticated tray models, e.g. with plug flow in the gas phase are not considered because of the preliminary character of this study. Gas and liquid phase back-mixing between trays as well as pressure drop over the trays are neglected. Non-ideality of the gas phase has not been considered. The mass and heat transfer parameters ( $k_l$ ,  $k_g$ ,  $a$ ,  $h_l$ ,  $C_F$ ,  $\rho$ ) are considered equal for all trays of the absorber. Physical parameters like viscosity, diffusivity, equilibrium constants and partition coefficients are taken as a function of the temperature on each tray.

The calculation starts with an overall mass balance over the column. For this purpose a  $\text{CO}_2$  concentration in the treated gas,  $y_{\text{CO}_2}^{n+1}$ , has to be specified and then the treated gas flow,  $\Phi_g^{n+1}$ , can be calculated by:

$$\Phi_g^{n+1} = \frac{\Phi_g^1 (1 - y_{\text{CO}_2}^1)}{1 - y_{\text{CO}_2}^{n+1}} \quad (1)$$

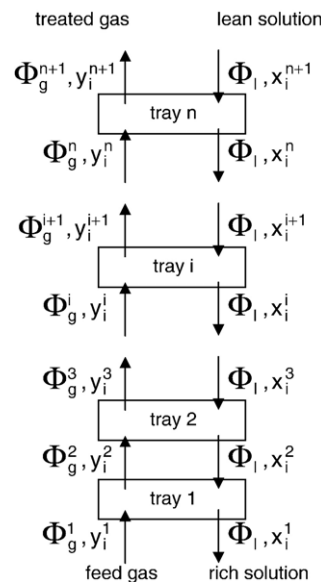


Fig. 1. Scheme for a tray absorber.

The composition and the flow of the treated gas are fixed now. Next, the liquid volumetric flow rate in the column is calculated in such a way that the rich solution leaving the column at tray 1 is loaded with acid gases to a preset, desired value, which is defined by the approach factor:

$$\alpha_{\text{CO}_2}^1 = \frac{[\text{CO}_{2,\text{tot}}]_1^1}{[\text{Amine}_{\text{tot}}]} = \frac{\text{Approach} \cdot [\text{CO}_{2,\text{tot}}]_{1,\text{eq}}^1}{[\text{Amine}_{\text{tot}}]} \quad (2)$$

$[\text{CO}_{2,\text{tot}}]$  and  $[\text{Amine}_{\text{tot}}]$  refer to the total concentrations of the respective components in both reacted and unreacted form.

The liquid flow is obtained from a total acid balance:

$$\Phi_1 = \frac{\Phi_g^1 [\text{CO}_2]_g^1 - \Phi_g^{n+1} [\text{CO}_2]_g^{n+1}}{\alpha_{\text{CO}_2}^1 [\text{Amine}_{\text{tot}}] - [\text{CO}_{2,\text{tot}}]_1^{n+1}} \quad (3)$$

In which all gas phase concentrations are expressed in  $\text{mol/m}^3$ . It is assumed that  $\Phi_1$  is constant over the column. From the overall mass balance the total acid gas concentration in the rich, outlet solution is calculated:

$$[\text{CO}_{2,\text{tot}}]_1^1 = \frac{\Phi_g^1 [\text{CO}_2]_g^1 - \Phi_g^{n+1} [\text{CO}_2]_g^{n+1}}{\Phi_1} + [\text{CO}_{2,\text{tot}}]_1^{n+1} \quad (4)$$

The heat capacities of the gas and the liquid can, depending on the process conditions, be of the same order of magnitude and therefore an energy balance has to

be incorporated in the model. The overall energy balance over the absorber is solved, according to the well-mixed assumption, with:

$$T_g^{n+1} = T_l^{n+1} \quad (5)$$

which means that the temperature of the top tray equals that of the lean amine solution introduced. This enables the calculation of the temperature of the rich solution, provided that gas and liquid inlet temperatures are specified:

$$T_l^1 = \frac{(T_g^1 - T_g^{n+1})\Phi_g^1 \rho_g C_{p,g}}{\Phi_l^1 \rho_l C_{p,l}} + \frac{\Delta H_{CO_2} ([CO_{2,tot}]_1^1 - [CO_{2,tot}]_1^{n+1})}{\rho_l C_{p,l}} + T_l^{n+1} \quad (6)$$

The  $\Delta H$  term represents the sum of the heats of both reaction and absorption. The gas and liquid compositions and conditions at the absorber bottom are now fixed and provide the starting point for the tray-to-tray calculations.

In order to solve the tray heat balance, thermal equilibrium is assumed between the gas and liquid flows leaving the tray:

$$T_g^{i+1} = T_l^i \quad (7)$$

At the absorber top, this equation is contradictory to the assumption for the overall heat balance expressed above ( $T_g^{n+1} = T_l^{n+1}$ ). This discrepancy is, however, negligible because  $T_l^{n+1} \cong T_l^{n+1}$ .

Now, as the gas temperature on the bottom tray 1 ( $T_g^2 = T_l^1$ ) is known, the liquid phase equilibrium constants, Henry coefficients, and gas and liquid phase diffusivities are calculated. The liquid phase composition, more specifically the concentrations of unreacted  $CO_2$  and amine, is obtained by means of the equilibrium model (described in Section 2.2).

Next,  $CO_2$  gas phase concentrations at tray 1, i.e. in the gas leaving tray 1, are estimated. Subsequently, gas phase concentrations are calculated, so that the absorption driving forces are now known. The molar flux ( $J_{CO_2}$ ) is calculated using a micro/flux model (see Section 2.3).

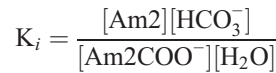
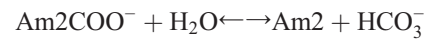
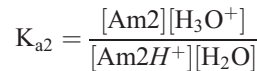
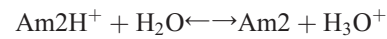
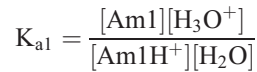
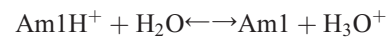
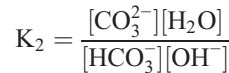
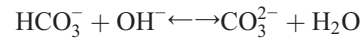
After the first estimation of the gas phase concentration and the subsequent molar flux calculations, tray iteration proceeds using a direct substitution method for the first iteration and a Regula-Falsi procedure for the remaining iteration steps, until the following convergence criteria is satisfied within the desired accuracy (usually <0.01% error):

$$J_{CO_2} a V_{tray} = \Phi_g^2 [CO_2]_g^2 = \Phi_g^1 [CO_2]_g^1 \quad (8)$$

Using mass and heat balances for tray 1,  $[CO_{2,tot}]_1^2$  and  $T_l^2$  are then calculated. The tray-to-tray procedure continues until the  $CO_2$  specification is met at tray n.

## 2.2. The chemical equilibrium model

For the calculation of the equilibrium composition of the aqueous solution it is necessary to solve simultaneously the following set of independent equilibrium equations:



Besides this set of equilibrium equations, also the charge (to assume electro-neutrality),  $CO_2$ , water and amine balances have to be solved simultaneously. In this equilibrium module no allowance has been made for non-ideal behavior of the liquid phase.

The equilibrium concentrations of  $CO_2$  in the gas phase are calculated from the respective liquid phase concentrations and solubility constant defined by:

$$m_i = \frac{[i]_{l,eq}}{[i]_{g,eq}} \quad (9)$$

This dimensionless solubility can be calculated from the Henry coefficient:

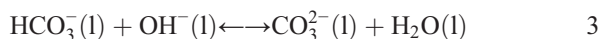
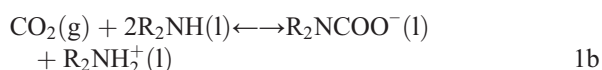
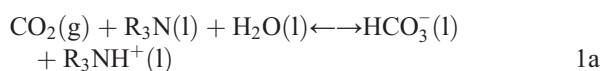
$$m_i = \frac{He_i}{RT} \quad (10)$$

Physical and chemical, kinetic and equilibrium constants used for the model calculations are taken from Versteeg et al., 1996.

### 2.3. The micro/flux model

The mass transfer model describes the absorption of CO<sub>2</sub> in an aqueous solution of a mixture of a tertiary and a primary/secondary alkanolamine (Versteeg et al., 1989, 1990). The absorption rates are calculated in combination with the concentration profiles near the gas–liquid interface for all reactants and products.

In this absorption model the system of reaction equations given in Section 2.2 is restructured to the following system of six reaction equations:



Where (g) indicates gas phase and (l) liquid phase respectively.

The reactions [3], [4] and [5] can be regarded as infinitely fast equilibrium reactions (Danckwerts, 1970) and therefore in the liquid phase these reactions are at equilibrium.

The forward reaction between CO<sub>2</sub> and the tertiary amine is a second order reaction (Versteeg and van Swaaij, 1988a) and can be described according to:

$$R_{\text{CO}_2} = k_{1,1}[\text{CO}_2][\text{R}_3\text{N}] \quad (11)$$

The forward reaction between CO<sub>2</sub> and the primary/secondary amine is a complex reaction (Versteeg and van Swaaij, 1988b) which can be described according to the zwitterion mechanism (Danckwerts, 1979). In the mass transfer model this reaction is approximated by a second order reaction, similar to Eq. (11) and the second order

reaction rate constant is estimated with the following equation:

$$k_{1,1} = \frac{1}{\frac{1}{k_2} + \frac{1}{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + \sum_{i=1}^n k_{\text{Am},i}[\text{Amine}_i]_{\text{free}}}} \quad (12)$$

It should be noted that according to the reaction mechanism all the amines present in the solution contribute to the deprotonation of the zwitterion. However, for MEA this expression is reduced to

$$R_{\text{CO}_2} = k_2[\text{CO}_2][\text{MEA}] \quad (13)$$

as for this alkanolamine the formation of the zwitterion is the rate determining step (Versteeg and van Swaaij, 1988b).

The forward reaction [2] between CO<sub>2</sub> and the hydroxyl ion is a second order reaction (Pinsent et al., 1956) and can be described according to:

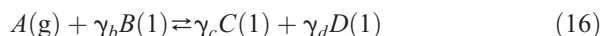
$$R_{\text{CO}_2} = k_{1,1}[\text{CO}_2][\text{OH}^-] \quad (14)$$

The rates of the reverse reactions are estimated from the assumption that at equilibrium the net reaction rate is equal to zero leading to:

$$K_{\text{eq}} = \frac{k_{\text{fwd}}}{k_{\text{back}}} \quad (15)$$

In the gas phase the mass transfer is described according to the stagnant film model (Whitman, 1923) and for the liquid phase Higbie's penetration model (Higbie, 1935) is used.

The problem considered is mass transfer accompanied by reversible chemical reactions of general order with respect to both reactants and products. The description of the absorption model and the numerical treatment is illustrated for a single reversible reaction:



with the following overall reaction rate equation:

$$R_a = k_{R,m,n,p,q}[A]^m[B]^n[C]^p[D]^q - k_{R,r,s,t,v}[A]^r[B]^s[C]^t[D]^v \quad (17)$$

It is clear that for systems with parallel and/or consecutive reactions the number of reactions will increase.

Usually for gas–liquid systems most reactions can be expressed with sufficient accuracy with a reaction rate expression similar to Eq. (16) and therefore this expression was used in this model.

The mass transfer in the gas phase is described with the stagnant film model while for the liquid phase the penetration model is used, as the penetration model is expected to be the most realistic one in describing gas–liquid absorption.

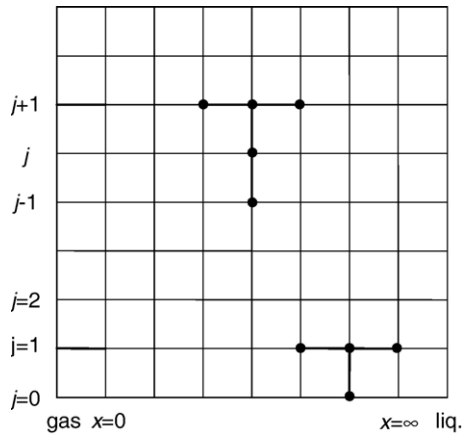


Fig. 2. Discretisation scheme.

For the penetration model the balances for each species for the phenomenon mass transfer followed by a chemical reaction yields the following set of equations:

$$\frac{\partial r}{\partial t} = D_a \frac{\partial^2 [A]}{\partial x^2} - R_a \quad (18)$$

$$\frac{\partial [B]}{\partial t} = D_b \frac{\partial^2 [B]}{\partial x^2} - \gamma_b R_a \quad (19)$$

$$\frac{\partial [C]}{\partial t} = D_c \frac{\partial^2 [C]}{\partial x^2} + \gamma_c R_a \quad (20)$$

$$\frac{\partial [D]}{\partial t} = D_d \frac{\partial^2 [D]}{\partial x^2} + \gamma_d R_a \quad (21)$$

These four coupled non-linear partial differential equations must be solved numerically because an analytical solution method is not available. To be solved uniquely the four non-linear partial differential Eqs. (17)–(21) require one initial and two boundary conditions respectively. The initial condition is given by:

$$t = 0 \text{ and } x \geq 0, [A] = [A]_0, [B] = [B]_0, [C] = [C]_0, [D] = [D]_0 \quad (22)$$

where the concentrations  $[i]_0$  satisfy  $R_a = 0$  in Eq. (17). The boundary condition for  $x = \infty$  can also be derived with the assumption of chemical equilibrium for the bulk of the liquid for a given solute loading:

$$t > 0 \text{ and } x = \infty, [A] = [A]_0, [B] = [B]_0, [C] = [C]_0, [D] = [D]_0 \quad (23)$$

Note that the application of Eqs. (22) and (23) is only valid if the equilibrium composition is used (see Section 2.2).

Table 1  
Data used for all cases

Parameter	Value	Unit
Total pressure	70	Bar
CO <sub>2</sub> inlet pressure	11.5	Bar
CO <sub>2</sub> outlet pressure (spec.)	140	Pa
Gas inlet flow	237	Nm <sup>3</sup> /s
Amine	MDEA (aqueous)	–
Accelerator amine	(see Table 3)	–
Accelerator amount	(see Table 3)	mol%
Total amine concentration	3000	mol/m <sup>3</sup>
Gas inlet temperature	12	°C
Liquid inlet temperature	45	°C
Liquid inlet loading	0.0073	mol CO <sub>2</sub> /mol amine
Approach	(see Table 2)	%
Liquid inlet flow	(see Table 2)	m <sup>3</sup> /s
Liquid mass transfer $k_l$	(see Table 2)	m/s
Gas mass transfer $k_g$	(see Table 2)	m/s
Specific contact area $a$	(see Table 2)	m <sup>2</sup> /m <sup>3</sup>
Tray volume $V_{\text{tray}}$	(see Table 2)	m <sup>3</sup>
Liquid phase density	1020	kg/m <sup>3</sup>
Liquid phase heat capacity	3800	J/kgK
Gas phase molar weight	20.6	g/mol
Gas phase heat capacity	2350	J/kgK
Reaction + absorption enthalpy	90.0	kJ/mol

The second associated boundary condition is obtained by assuming that the species  $B$ ,  $C$  and  $D$  are non-volatile and that the flux of component  $A$  from the gas phase is equal to the flux of component  $A$  to the liquid phase. The use of the latter assumption instead of assuming that  $[A] = [A]_i$  at  $x = 0$  is convenient in view of the applicability of the model for cases where a part of the resistance against mass transfer is situated in the gas phase. This is the case in the asymptotic situation of instantaneously fast reactions:

$$\begin{aligned} -D_a \left( \frac{\partial [A]}{\partial x} \right)_{x=0} &= k_g ([A]_{g,\text{bulk}} - [A]_{g,i}) \left( \frac{\partial [B]}{\partial x} \right)_{x=0} \\ &= \left( \frac{\partial [C]}{\partial x} \right)_{x=0} = \left( \frac{\partial [D]}{\partial x} \right)_{x=0} = 0 \end{aligned} \quad (24)$$

In the model the concentration profiles are time-dependent: they develop a solution of a system of coupled non-

Table 2  
The three base cases

Parameter	Base case 1	Base case 2	Base case 3	Unit
Approach	70	40	10	%
Liquid inlet flow	1.1	1.3	1.8	m <sup>3</sup> /s
Liquid mass transfer $k_l$	$2.023 \cdot 10^{-4}$	$2.011 \cdot 10^{-4}$	$1.963 \cdot 10^{-4}$	m/s
Gas mass transfer $k_g$	$1.010 \cdot 10^{-3}$	$9.926 \cdot 10^{-4}$	$9.370 \cdot 10^{-4}$	m/s
Specific contact area $a$	1830	1804	1724	m <sup>2</sup> /m <sup>3</sup>
Tray volume $V_{\text{tray}}$	3.285	3.484	4.137	m <sup>3</sup>



Table 3  
Data varied from base case

Parameter	Value	Unit
Accelerator amine	MEA: mono-ethanol-amine	–
	MMEA: mono-methyl-ethanol-amine	
	DGA: di-glycol-amine	
	DEA: di-ethanol-amine	
	DIPA: di- <i>iso</i> -propanol-amine	
	AMP: 2-amino-2-methyl-1-propanol amine	
Accelerator amount	0.0, 1.0, 2.5, 5.0, 7.5 and 10.0	mol%

linear parabolic partial differential equations subject to specified initial and two point boundary conditions. The implicit discretisation method used is known as the [Baker and Oliphant \(1960\)](#) discretisation. For the time derivative a three-point backward discretisation is used (with superscript  $j$  indicating the time level) leading to ( $i=A,B,C,D$ ):

$$\frac{\partial[i]}{\partial t} \rightarrow \frac{3[i]^{j+1} - 4[i]^j + [i]^{j-1}}{2\Delta t} \quad (25)$$

The finite difference form of the reactor model thus leads to relations between concentrations in five grid points (two additional points are used to describe the diffusion), clustered as “molecules” as shown in [Fig. 2](#). Only for  $j=0$  these molecules are not possible, because no grid points with time index  $-1$  exist. Therefore in the first step a two-point backward discretisation (Euler) is used at cost of lower order truncation error.

The absorption models that describe mass transfer accompanied by complex reversible reactions have been validated experimentally in a stirred cell model contactor ([Danckwerts, 1970](#)). The absorption of  $\text{CO}_2$  or  $\text{H}_2\text{S}$  in aqueous alkanolamine solutions or aqueous

solutions of mixtures of various alkanolamines was used. For these systems the physical and chemical constants and parameters respectively are well known from literature. These experiments were carried out and published by [Versteeg et al. \(1989, 1990\)](#). From their results it could be concluded that the developed micro models simulated the experimentally observed absorption rates satisfactory over a wide range of conditions.

### 3. Simulation results

This section presents the results of a study of the effect on column performance of adding a primary/secondary amine (accelerator) to an aqueous absorption solution with a tertiary amine.

For this study three base cases are defined based on a practical case that was received from [Geuzebroek, 2004](#). The three base cases differ only in the (arbitrary chosen) approach factor (10%, 40% and 70%).

This results in three different liquid flows (set by Eqs. (2) and (3) in Section 2) and therefore different hydrodynamics and mass transfer parameters. For each of the base cases the mass transfer parameters ( $k_L$ ,  $k_g$ ,  $a$ ,  $V_{\text{tray}}$ ) were taken from [Geuzebroek, 2004](#). These values were averaged and used for the corresponding base cases.

The data used for the three base cases is presented in the tables below ([Tables 1 and 2](#)). The various accelerators tested and their concentrations are presented in [Table 3](#).

Next, the required number of trays for each of the base cases was determined by the absorber model described in Section 2.

The performance of various accelerators was tested at 40% approach. [Fig. 3](#) shows the number of trays required

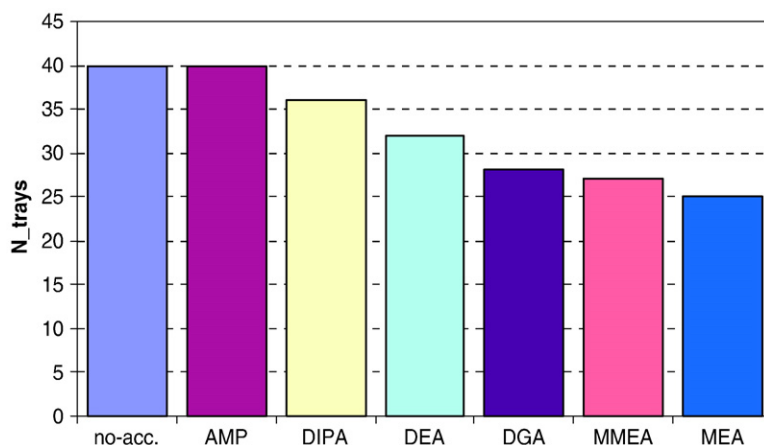


Fig. 3. Number of trays required with various accelerators (base case 2 (40% approach) and 2.5 mol% accelerator).

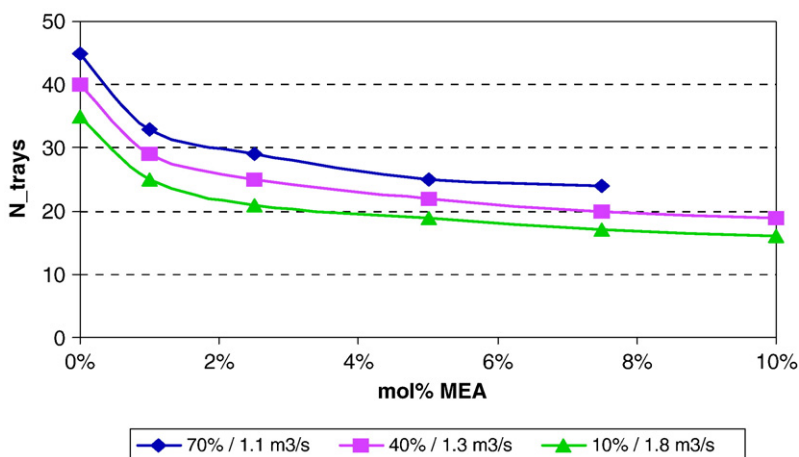


Fig. 4. Number of trays required with MEA as accelerator at different amounts and three different approaches (70%, 40% and 10%).

for the absorber defined by base case 2 and using various accelerators at 2.5 mol%.

From Fig. 3 it is clear that mono-ethanol-amine (MEA) performs best. Without accelerator 40 trays are required, while after adding 2.5 mol% MEA only 25 trays are required. This means that the column size is reduced almost two times.

Mono-methyl-ethanol-amine (MMEA) and di-glycol-amine (DGA) also perform relative good (27 and 28 trays required respectively).

Di-ethanol-amine (DEA) and di-*iso*-propanol-amine (DIPA) show moderate results with 32 and 36 required trays respectively.

It is also clear that adding 2-amino-2-methyl-1-propanol amine (AMP) does not give any improvement at all.

Using MEA as accelerator, the results of simulations calculating the number of required trays at different approaches are given in Fig. 4.

It is clear that the improvement of column performance by adding an accelerator is obtained at all approaches (see Eq. (2), Section 2). It is also clear that adding more accelerator give smaller absorption columns, however, most profit is obtained for the first 3 mol% of accelerator:

- Adding 2.5 mol% of MEA at 70% approach lowers the required number of trays from 45 to 29, thereby saving 16 trays. Adding another 2.5 mol% saves only 4 more trays.
- Adding 2.5 mol% of MEA at 40% approach lowers the required number of trays from 40 to 25, thereby

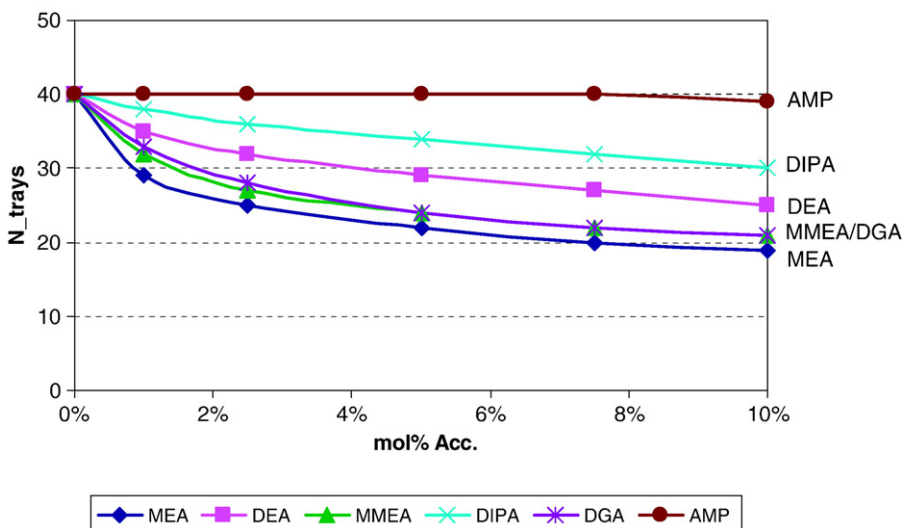


Fig. 5. Number of trays required with various accelerators at different concentrations (base case 2, 40% approach).



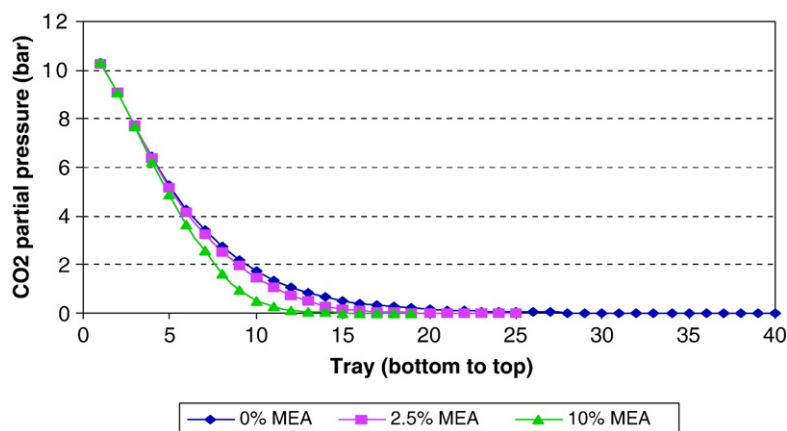


Fig. 6. Axial pressure profile at three MEA dosages (base case 2, 40% approach).

saving 15 trays. Adding another 2.5 mol% saves only 4 more trays.

From Fig. 5 it can be concluded that the qualitative behavior found in Fig. 4 is not only found for MEA as accelerator, but also with other tested accelerators. From Fig. 5 it is also clear that adding AMP has no effect at all, not even at high concentrations. This is due to the fact that the reaction between AMP and  $\text{CO}_2$  is spatially hindered.

MEA is again found to be the best accelerator. It performs best at all simulated accelerator concentrations.

Below some column profiles are shown as a function of a number of (process) parameters of interest. This gives more insight in the way the accelerator works.

Fig. 6 shows the axial partial pressure profiles of  $\text{CO}_2$ . From these profiles it is clear that the performance of the bottom trays (1–4) is the same for all cases. The profit of the accelerator is obviously obtained at the top trays.

The number of trays required for taking out the last amounts of  $\text{CO}_2$  at the top is reduced substantially by adding a small amount of accelerator (MEA).

For this specific case it can be concluded that the acceleration is only achieved below a  $\text{CO}_2$  partial pressure of about 4–5 bar.

Fig. 7 shows the axial temperature profile for the same three cases as shown in Fig. 6. As expected there is a close correlation in shape of the curves presented in Figs. 6 and 7. This is due to the obvious fact that temperature effect will only occur at trays where chemical reactions and absorption take place. The temperature is influenced by the resultant enthalpy of exothermic and endothermic reactions.

The differences between the temperature profiles are very small and will not influence the column performance significantly. Besides, in the previous paragraph it was shown that the accelerator is mainly influencing the performance of the top trays. This part of the column is operated almost isothermally.

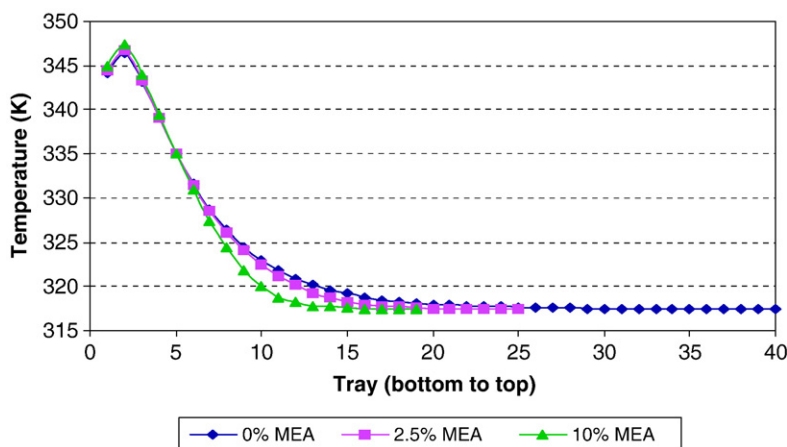


Fig. 7. Axial temperature profile at three MEA dosages (base case 2, 40% approach).

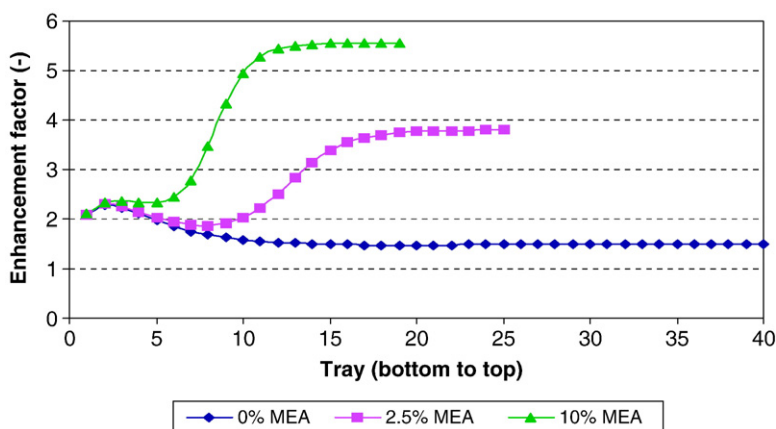


Fig. 8. Axial profile of enhancement factor at three MEA dosages (base case 2, 40% approach).

Fig. 8 demonstrates that adding small amounts of accelerator has a large effect on the enhancement of mass transfer due to chemical reaction. The enhancement factor is defined as the ratio between the molar flux including chemical reaction and the molar flux excluding chemical reaction (diffusion only). At the bottom of the column the enhancement factor is equal for all cases (the entire amount of accelerator has reacted), but at the top of the column large differences exist. At the top trays only small amounts of  $\text{CO}_2$  are removed, which ensures long “lifetime” of the accelerator.

Adding only 2.5 mol% of MEA increases the enhancement factor from 1.5 to almost 4. This means that the mass transfer on the top trays is increased 2.5 times! This effect fully explains that the required number of trays is much smaller when adding the accelerator.

Fig. 9 shows the concentration profiles of  $\text{CO}_2$  near the gas–liquid interface for the three cases discussed in

the precious paragraphs. It is clear that the gradient at the gas–liquid interface ( $x=0$ ) is steeper if more accelerator is added. A steeper gradient corresponds to a larger mass transfer flux. This thus confirms the results found in the Fig. 8.

### 3.1. Accelerator optimization

In the preceding part of this paper, six different accelerators were tested (MEA, MMEA, DGA, DEA, DIPA and AMP). These accelerators were chosen because of the availability of reaction kinetics, physical- and chemical properties in open literature. MEA was found to be the most successful accelerator.

However, it is possible that other existing or non-existing (fictitious) amines perform even better than MEA. To predict the performance of the optimal accelerator and see if it performs much better than

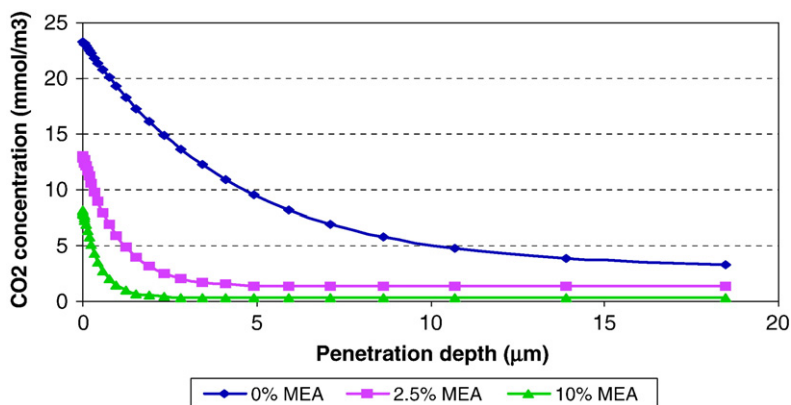


Fig. 9. Liquid phase concentration profile of  $\text{CO}_2$  near the gas–liquid interface at the end of the contact time defined by the Higbie penetration model at three MEA dosages (base case 2, 40% approach).

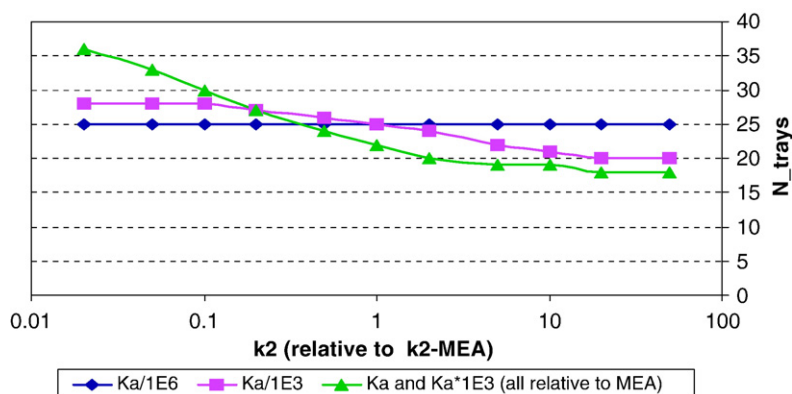


Fig. 10. Performance of fictitious accelerators estimated by adjusting the major kinetic data (based on base case 2, 40% approach, with 5.0 mol% of accelerator) The triangle at  $k_{2,\text{relative}}=1$  corresponds to base case 2 with 5.0 mol% MEA (22 trays).

MEA or not, some additional calculations have been performed by adjusting the kinetic data in the databank.

An accelerator is characterised by two main kinetic parameters:

$$k_{1,i} = \frac{1}{\frac{1}{k_2} + \frac{1}{k_{H_2O}[H_2O] + \sum_{i=1}^n k_{Am,i}[Amine_i]_{\text{free}}}} \stackrel{\text{MEA}}{=} k_2$$

and

$$k_{a2} = \frac{[Am_2][H_3O^+]}{[Am_2H^+][H_2O]}$$

Therefore, column calculations have been performed using base case 2 with 5 mol% MEA as a base case (22 trays) and then  $k_2$  and  $K_{a2}$  were varied (in the computer program the parameter  $K_{CO_2}$  had to be varied because it depends on  $K_{a2}$ ).

The results are shown in Fig. 10. It is clear that increasing  $k_2$  decreases the number of trays required. It can however be concluded that a significantly better performing accelerator than MEA seems not to exist.

For the case presented in Fig. 10, 5 mol% MEA results in 22 trays, and an optimal accelerator requires about 18 trays. Without accelerator the number of required trays is 40 (see Fig. 3). Thus, using MEA saves 18 trays and a perfect accelerator would save only 4 more trays.

#### 4. Conclusions

From the simulations the following is concluded:

- Adding a suitable accelerator to aqueous MDEA solutions improves the column performance significantly for all three tested approaches;

- From the simulated accelerators MEA performs best and reduces the required number of trays up to two times; MMEA and DGA also perform relatively good; AMP does not have any effect on column performance;
- Only a small amount of accelerator is required. Adding only 1 mol% of MEA to an aqueous MDEA solution was able to reduce the required number of trays from 40 down to 29, 2.5 mol% of MEA was able to reduce the required number of trays from 40 down to 25;
- Adding small amounts of MEA has a large effect on the enhancement factor of mass transfer due to chemical reaction only at the top of the absorber column;
- For the investigated cases, MEA has a performance that is close to the performance of an optimal (fictitious) accelerator.

It must be noted that for the tray simulations physical–chemical constants of the solvent mixture have been estimated from data published in literature.

Furthermore, in this study the absorption behavior is examined theoretically only. Practical phenomena like scaling, foaming, corrosion, etc. are not taken into account. Also no attention is paid to the influence of the solvent selected on regeneration costs. Selecting the optimal solvent, the possible gain in capital expenditure should be evaluated against possible loss in operational expenditure due to increasing energy losses of regeneration.

#### Nomenclature

##### Normal symbols

$a$	Specific gas–liquid interface $\text{m}^2 \text{m}^{-3}$
$C_p$	Heat capacity $\text{J kg}^{-1} \text{K}^{-1}$
$D$	Diffusion coefficient $\text{m}^2 \text{s}^{-1}$
$h$	Heat transfer coefficient $\text{W m}^{-2} \text{K}^{-1}$

He	Henry coefficient $\text{J mol}^{-1}$
$J$	Mass transfer flux $\text{mol m}^{-2} \text{s}^{-1}$
$k_g$	Gas phase mass transfer coefficient $\text{m s}^{-1}$
$k_l$	Liquid phase mass transfer coefficient $\text{m s}^{-1}$
$K$	Equilibrium constant
$K$	Reaction rate constant
$m$	Partition coefficient –
$R$	Reaction rate $\text{mol m}^{-3} \text{s}^{-1}$
$R$	Gas constant $(8.314) \text{ J mol}^{-1} \text{ K}^{-1}$
$t$	Time s
$T$	Temperature K
$x$	Molar fraction liquid phase
$x$	Position in penetration model m
$y$	Molar fraction gas phase
$\Delta H$	Enthalpy of reaction and absorption $\text{J mol}^{-1}$
$V_{\text{tray}}$	Volume of liquid on a tray $\text{m}^3$

#### Greek symbols

$\alpha$	Liquid loading $\text{mol mol}^{-1}$
$\gamma$	Stoichiometry number
$\rho$	Density $\text{kg m}^{-3}$
$\Phi$	Gas flow $\text{mol/s}$

#### Subscripts

Am	Amine
back	Backward reaction
eq	Equilibrium
fwd	Forward reaction
g	Gas phase
l	Liquid phase
I	Component I
j	Time line index
tot	Total, reacted as well as unreacted

#### Superscripts

$n$	Tray number
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